

Prospective Catalytic Structured Converters for NH_3 -SCR of NO_x from Biogas Stationary Engines: In Situ Template-Free Synthesis of ZSM-5 Cu Exchanged Catalysts on Steel Carriers

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Abstract The main objective of this study is to develop highly active catalyst and its preparation method that would meet the requirements of steel carriers for short-channel structured converters for NO_x abatement from stationary biogas engines. The in situ synthesis was applied to deposit a series of Cu-exchanged MFI zeolite (ZSM-5) on kanthal sheets. The samples differ in preparation conditions: organic template assisted and template-free synthesis, Si/Al ratio and catalyst carrier pretreatment (calcined vs. non-calcined). Dip-coating method was used as a reference to compare loading efficiency. In order to evaluate preparation quality and purity of resulting structure the samples were examined by XRD and SEM/EDS at various stages of preparation. For the assessment of mechanical endurance of the deposited catalyst layers the ultrasonication method was used. The results demonstrated high depositing efficiency of the in situ synthesis as well as high activity and selectivity of the Cu-exchanged MFI samples prepared without costly organic template.

Keywords NH_3 -SCR · ZSM-5 · MFI synthesis · Cu-exchanged zeolites · Structured reactors · Biogas engines

1 Introduction

The motivation of this study arises from the interest in biogas as a fuel for internal combustion engines. Depending on the process, biogas may be obtained from biomass as a producer gas with high nitrogen content or a syngas with low nitrogen content [1]. The producer gas may then be used as an alternative fuel in stationary gas engines to supply energy in the form of electricity and heat at a local level. The composition of exhaust gases emitted by combustion differ between the producer gas and natural gas mainly in the emission factor of NO_x which exceeds 605 and 193 g/GJ, respectively [2].

Despite the fact that there are a great many working solutions for abatement of exhaust gases from stationary sources and from engines, mainly based on multi-channel ceramic monoliths, the development of the biogas engine technologies creates an opportunity to explore more effective and economic clean-up installations. To reduce NO_x emissions, the well-established process of selective catalytic reduction (SCR) with NH_3 or urea could be used as described for example in [3, 4] but the main drawback is the installation size which is connected with the huge size of urea or ammonia dosage systems often exceeding in size the biogas engine itself. Additionally, due to new environmental regulations called Waste Incineration Directive the process efficiency will have to be increased by prolonging monolithic converter. An interesting alternative to NH_3 -SCR could be the process based on the use of alternative reducing agents which are already included in biogas. One of the other

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opportunities is the application of “short channel structures” (as opposed to long multi-channel monoliths) in form of wire meshes or sinusoidal stripes as catalyst carriers and reactor fillers [5, 6]. The heat and mass transfer characteristics of wire gauzes and sinusoidal structures are comparable with those in packed beds, whilst being substantially higher than those obtained in monolith supports as described for example in [7, 8]. There the flow resistance per unit bed length was ranked in the following order: packed bed > wire gauze > monolith, which does not mean that the overall pressure drop would be higher in the same ranking, as that would depend on the length of each bed to achieve the necessary conversion. Indeed, the enhanced mass transport in such reactors gives rise to substantial reduction of the reactor length even up to 50 times with reasonable pressure drop as described in [7]. It is also worth emphasizing that to exploit the enhanced rates of mass transfer in short channel structures, active catalysts need to be employed, which is the main focus of our current research.

A serious drawback in the use of zeolites as catalysts for NH_3 -SCR is their inadequate hydrothermal stability under the conditions of operation, already recognized in recent reviews [9, 10]. Low hydrothermal stability of majority of zeolites is claimed to be surpassed by the process of ultra-stabilization which was discovered for Y zeolite and also investigated in our previous paper for Cu-USY [11]. Recently small pore size zeolite—SSZ-13 of chabazite (CHA) structure has received a lot of attention due to its high hydrothermal stability, high activity in SCR and high selectivity to N_2 [12, 13]. Also, the catalyst producers has begun to offer zeolitic catalyst designed for higher temperature operation window than the classic vanadia based SCR catalysts. An example of this can be the commercial ZNXTM catalyst which operates over a higher temperature range (350–590 °C), and demonstrates low NH_3 slip and high sulfur resistance [4, 14].

The choice of copper exchanged ZSM-5 (MFI) zeolites in this study is mainly because they have been extensively studied before. The ZSM-5 zeolites exchanged with Cu demonstrated remarkable activity not only in the reduction of nitrogen oxides with NH_3 (NH_3 -SCR) [15, 16] but also in the direct decomposition of NO [17, 18]. This can be a good starting point to explore further the synthesis and structure correlations as well as the principles of hydrothermal stability of zeolites. Through our research we hope to design zeolitic catalysts of high activity and high hydrothermal stability that would meet the requirements of short channel structures. However, in our opinion this can be achieved only through deeper understanding of structure-sensitivity relationships of existing zeolites of known structures. The particular aims to achieve in this survey are:

- template-free synthesis of active ZSM-5 based catalytic material with possibly highest Si/Al,

- exploring depositing efficiency during in situ synthesis of zeolites on metallic plates, which are to be used as model catalyst carriers for further applications in structured reactors,
- evaluating catalytic performance of obtained catalysts with particular reference to the zeolitic material obtained without the use of organic template.

2 Experimental

2.1 Samples

Kanthal plates were used as a model catalyst carriers for further application as structured reactor fillers. Prior to zeolite depositing the kanthal support was cleaned with acetone and pre-calcined at 1000 °C for 48 h producing $\sim 1 \mu\text{m}$ alumina layer partially composed of $\alpha\text{-Al}_2\text{O}_3$ [19] (except a non-calcined sample, see Table 1). The alumina originates from oxidation of Al initially present in the support and is regarded as the matrix to which the aluminosilicates will anchor.

Crystal layers of ZSM-5 of various Si/Al ratios were grown in situ on pre-calcined or untreated metal surfaces. A sample obtained by the dip-coating method described in [11] was used as a reference to compare the efficiency of deposition. A brief overlook of the procedures and samples used in the study is provided in Table 1.

The in situ synthesis of ZSM-5 film on the steel support was carried out using mixture formulations adapted from published sources [20, 21]. Two synthesis methods were investigated: one with organic template (TPA-OH) and another without template. The reagents were obtained from Sigma-Aldrich: colloidal silica (Ludox LS, 30 %), sodium aluminate, tetrapropylammonium hydroxide (TPA-OH, 1 M), sodium silicate (10, 6 % Na_2O , 26, 5 % SiO_2), and sodium hydroxide (NaOH, 50 %). For the syntheses the demineralized water was used. The TPA-ZSM-5 synthesis expected to give the nominal 25–1 silica to alumina ratio was performed using the following molar ratios between substrates: $\text{Na}_2\text{O}:\text{SiO}_2:\text{Al}_2\text{O}_3:\text{H}_2\text{O} = 0.04:53:1:940$. The samples of Si/Al = 15 were prepared from correspondingly adjusted molar ratios of reactants. The template-free synthesis was carried out using ZSM-5 grains as crystallization nuclei. To launch a synthesis a mixture of a given proportion was transferred into a 300 cm³ Teflon-lined autoclave containing the home-made rack with vertically suspended catalytic supports. The temperature was increased within 1.5 h to 170 °C and the zeolite synthesis was continued for 30–50 h (depending on Si/Al ratio) under autogenous pressure. Upon verification of synthesis completeness by X-ray diffraction (XRD), the autoclave

Table 1 Preparation conditions and composition of ZSM-5 samples deposited kanthal plates and reference powder samples initial and exchanged with Cu cations

| Sample name | Support | Deposition method | Deposition conditions | Zeolite catalyst | | |
|-------------|---------|-------------------|-----------------------|------------------|-------|------------------------------|
| | | | | Si/Al | Cu/Al | Loading (g m ⁻²) |
| N | N | – | – | – | – | – |
| C | C | – | – | – | – | – |
| 15_SO | – | S | O | 15 | 0 | – |
| 15_SI | – | S | I | 15 | 0 | – |
| 25_SO | – | S | O | 25 | 0 | – |
| 15_CSO | C | S | O | 15 | 0.13 | 10 |
| 15_CSI | C | S | I | 15 | 0.25 | 13 |
| 25_CSO | C | S | O | 25 | 0.25 | 14 |
| 25_NSO | N | S | O | 25 | 0.35 | 101 |
| 37_CDO | C | D | O | 37 | 1.06 | 4 |

C calcined kanthal steel plate,
N non-calcined initial kanthal
 steel plate, *S* in situ synthesis,
D dip-coating, *O* organic
 template, *I* no template

content was discharged, the powder samples withdrawn, rinsed with deionized water and dried overnight at 110 °C as described in [22]. Afterwards they were calcined in air with the following ramp protocol: 4 °C min⁻¹ up to 400 °C, 1 °C min⁻¹ to 500 °C, dwell interval of 10 h followed by cooling mode at a rate 5 °C min⁻¹.

Zeolite crystals grown on kanthal plates were ion exchanged at room temperature with 0.1 M Cu(NO₃)₂ solution for 22 h under continuous stirring according to the procedure developed in [23]. Dip-coated samples were prepared by immersing the supports in the 20 wt% water suspension of a Cu-ZSM5 zeolite of a particle size ranging between 400–500 μm. The details can be found in our previous work [11]. The copper exchange procedure was the same as used for the ZSM-5 samples except the concentration of Cu(NO₃)₂ was 0.5 M. The coverage of a packing was determined by measuring mass of zeolite deposited on a support referred to its geometrical surface.

2.2 Catalyst Characterization and Performance

The synthesized coatings as well as the crystals obtained in bulk were examined by XRD for phase identification. The XRD data were collected by diffractometer (Xpert'Pro) using Cu Kα radiation in the range of 5–65° 2θ, step scanning at 0.02° 2θ per step and acquisition time of 1.5 s for each step.

The texture of deposited kanthal plates was studied using scanning electron microscopy equipped with electron analytical probe (SEM/EDS, Philips XL20). The amount of Cu was determined by UV/VIS quantitative analyses of its aqua-hydroxo complexes obtained upon dissolving zeolite in a concentrated NaOH solution.

The adherence of zeolite layer was evaluated by ultrasonication method according to the procedure given in [24]. The method relies on measuring weight loss caused by exposing the sample to ultrasonic treatment. The coated

kanthal plates were immersed in acetone inside sealed bottle, and subjected to ultrasonication (Bandelin, 35 kHz) for 1 h, then dried for 1 h at 110 °C. The difference in a sample mass before and after the ultrasonic treatment was used as a measure of mechanical stability of the zeolite layer attached to the steel support.

Catalytic activity of deposited samples (Table 1) was examined in SCR of NO with ammonia using temperature programmed surface reaction method (TPSR). The tests were performed in a microreactor (Hiden Analytical CAT-LAB-PCS) equipped with QMS (with Faraday and SEM detectors) positioned downstream of the reactor to analyze the effluent gases including NH₃, NO, NO₂, N₂O, N₂ and H₂O. Prior to the catalytic experiments, the catalyst was conditioned in 5 % O₂ in helium at 500 °C. Once the maximum temperature was reached the sample was cooled to the required experimental temperature. In all experiments helium was used as an inert (balance) gas and the total flow rate of 25 ml min⁻¹ was kept constant. Catalytic reactions were carried out in the temperature range 40–500 °C under atmospheric pressure of a reacting mixture containing: 2000 ppm NO, 2000 ppm NH₃ and 5 vol% O₂ in He. The amount of water vapour in the gases fed into the reactor was also measured and found to be about 300 ppm.

The calibration of the QMS for the NH₃-SCR reacting mixture, is a complex undertaking as cross-sensitivity of gas components at similar m/z values make their identification problematic [25]. The calibration procedure consisted of several steps. The pure gases were used (Air Products) and the following mass to charge m/z lines were considered: NO (30), NH₃ (17), H₂O (18), N₂O (44), NO₂ (46), N₂ (28). The calibration was performed using both the SEM and Faraday detectors. In the first approximation the sensitivity factors provided by the Hiden QMS library were used. Then the contribution of various lines was taken into account by solving a system of linear equations for the given m/z value. Upon further calibration cross-sensitivities

between NO, NO₂, N₂O, NH₃ and H₂O for corresponding m/z : = 30: NO (100 %), N₂O (40 %), NO₂ (100 %), m/z = 17: NH₃ (100 %), H₂O (38 %) were noted. Also, contribution of a specific gas component changed with operating pressure in the QMS chamber. The maximum scatter measured for the NO line for various calibration mixtures was 10 % and it corresponds to a maximum error of determination of NO conversion. For this study only two first calibration steps (sensitivity factors, contributions) were taken for the rough assessment of catalysts activity.

3 Results and Discussion

The results of depositing efficiency by mass increase and mechanical endurance of the prepared layers by ultrasonication are presented in Fig. 1. As can be inferred from the values representing zeolite loading related to the sample mass (steel substrate and zeolite) the most efficient depositing procedure (the highest zeolite deposit amount) was obtained by in situ synthesis. Among the in situ synthesized samples the most effective substrate occurred the non-calcined plate (30 wt%—three times more than the precalcined plate). The efficiency of the dip-coating method was around six times less than the in situ method on the non-calcined plates and twice less than on the calcined plates. The mechanical endurance of the in situ deposited layers measured by ultrasonication was comparable and three times higher than of the dip-coated samples as can be inferred from the pronounced mass loss observed for this sample (97 wt%).

The in situ synthesized zeolite samples both powder and deposited on kanthal plates (Table 1) were examined by X-ray powder diffraction (XRD) to verify their structure

and purity (Fig. 2a). The results obtained for powder samples (prior to Cu exchange, 15_SO, 15_SI, 25_SO) confirm formation of highly crystalline MFI zeolite, except the sample of Si/Al = 15 synthesized using organic template (15_SO) for which additional reflection at around $2\Theta = 10.1$ evidences mordenite impurity. Since the samples 25_NSO and 25_CSO deposited on calcined and non-calcined steel for unknown reasons showed the reflections mainly from the substrate (compare with samples N and C in Fig. 2a), the structure evaluation relied on the XRD pattern of the powder counterpart 25_SO. Finally, no difference in XRD patterns can be noted between initial and Cu-exchanged samples evidencing atomic dispersion of Cu within zeolite structure.

The surface morphology studied by SEM/EDS methods is presented in Fig. 2b. The EDS results confirmed the presence of Cu in the exchanged zeolite samples, even though the quantitative determination of Cu content relied on the UV–Vis spectrometric analyses. The general observation from SEM images is that the surface texture changes with Si/Al content and also the presence or absence of the organic template during the synthesis. The largest catalyst grains of around 3 μm were typical of the lower Si content (Si/Al = 15, 15_CSO and 15_CSI) in contrast to the samples of higher Si content (Si/Al = 25, 25_CSO, 25_NCO) which showed higher zeolite material dispersion with average grain size of around 1 μm . Despite similarities in morphologies of materials of the same Si/Al there are also differences between them. For the samples of Si/Al = 15 obtained with the template (15_CSO) the grains are spherical (15_CSO) while for those obtained without the template (15_CSI)—ellipsoidal.

3.1 Catalytic Performance

The catalysts are also compared in terms of their catalytic performance measured in TPSR experiments of NH₃-SCR of NO. Catalyst activity is expressed as NO conversion as a function of temperature in Fig. 3. For all the zeolite coated samples the selectivity towards N₂ was almost 100 %. Conversion values determined from NO and N₂ concentrations measured by QMS were almost the same, while the difference between NO and NH₃ conversion reached maximum 15 % (NH₃ conversion lower). This discrepancy results from the limited accuracy of analyses by QMS caused by cross-sensitivities of the measured signals of NO and NH₃. However, the difference in the conversion can be regarded as a gauge of the maximum error of the analytical method.

The general trend in conversion is the initial growth (to around 400 °C) and further decrease (up to 500 °C—the highest temperature used). It is worth noting that despite the highest depositing efficiency (Fig. 1), the 25_NSO

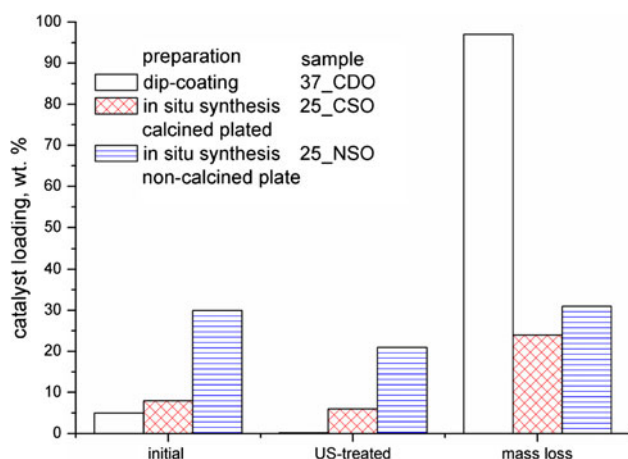


Fig. 1 Mechanical strength measurements of layers of zeolites deposited on kanthal plates (Table 1) performed using ultrasonic treatment 35 kHz for 1 h in acetone

Fig. 2 **a** XRD patterns in situ synthesized ZSM-5 samples with and without Cu; **b** SEM images of a series of Cu-exchanged ZSM-5 samples; all symbols as in Table 1

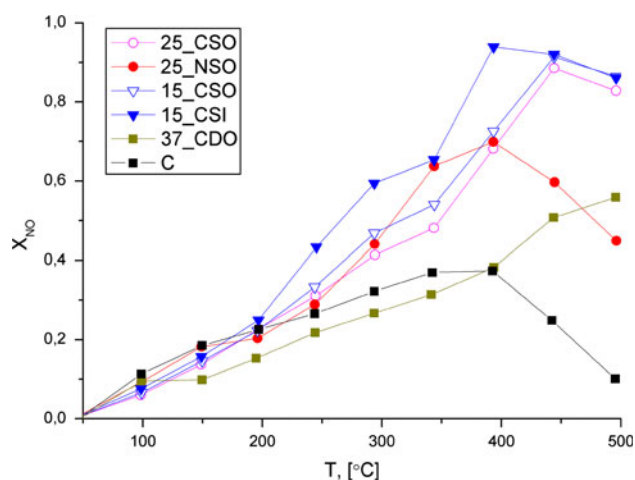
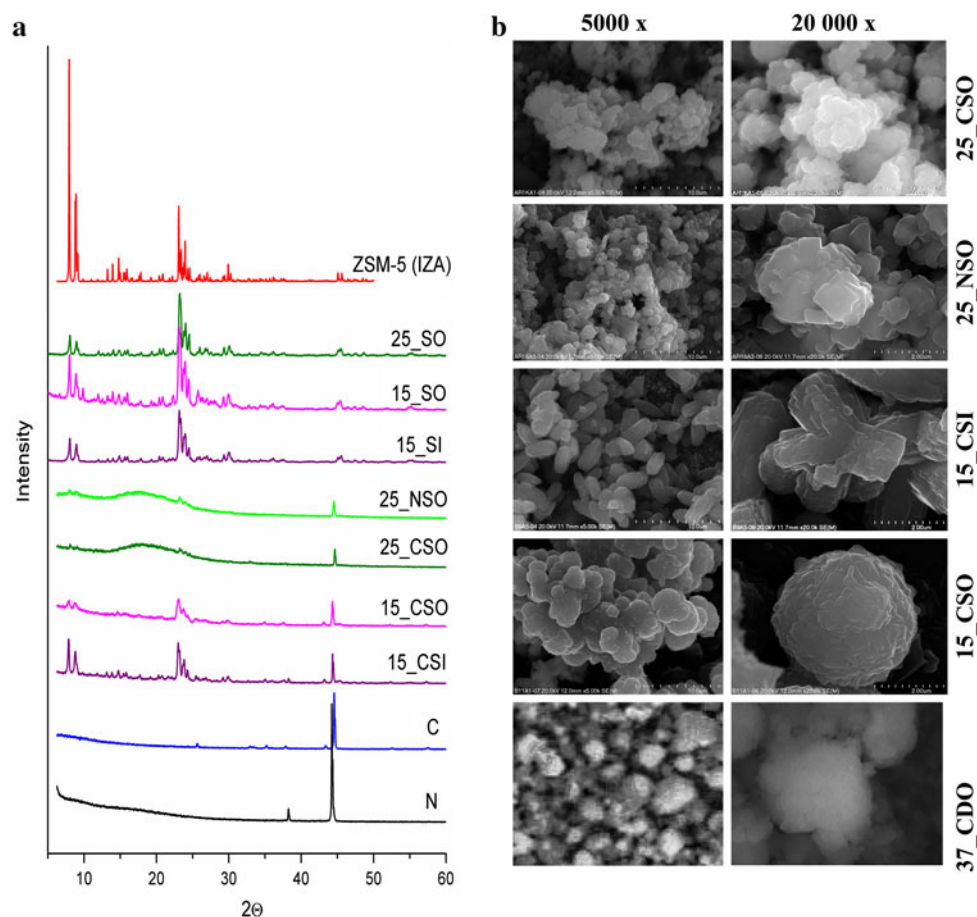


Fig. 3 TPSR results of activity evaluation of the series of deposited zeolitic MFI samples in SCR of NO by ammonia: X-conversion of NO

sample deposited on non-calcined steel sheets showed much less activity (max. conversion 70 % at 400 °C) than the 25_CSO counterpart deposited on precalcined steel. The qualitative QMS analyses of products showed partial oxidation of NH_3 to NO by the 25_NSO (also by the

reference C sample) above 400 °C. Most importantly, high activity and relatively high hydrothermal stability was observed for the samples deposited on pre-calcined steel sheets and among them the highest for the 15_CSI material prepared without organic template whose conversion was up to 20 % higher than that of its organic template counterpart 15_CSO in the temperature range from 250 to 400 °C. The sample prepared by dip-coating showed the lowest conversion (37_CDO) that did not have the same tendency upon temperature increase due to low and uneven coverage and low stability (Fig. 1) of the deposited layer.

The activity measurements indicate the structure sensitivity of the reaction connected with the catalyst dispersion (Fig. 2b), Si/Al content and preparation conditions (template assisted and template-free synthesis). However, the selection of the samples regarded for this study does not allow for differentiating between the above mentioned structural effects; the Si content impact cannot be separated from the preparation conditions and the presence of undesired phases or impurities. The observations made in this study are thus a starting point for further investigation of a structure-sensitivity effects with a particular stress on the highly active MFI materials obtained at low cost without organic template.

4 Conclusive Remarks

The achievement of this study is the template-free in situ synthesis of MFI zeolite directly on precalcined steel surface. Although obtained catalytic material exchanged with Cu cations was evaluated in SCR of NO using ammonia as a reducing agent, it can be regarded for other MFI catalyzed industrial processes. On the other hand the in situ depositing method of zeolites shows a lot of promise in efficient preparation and application of metallic structured reactors and among them short channel structures of enhance heat and mass transport properties. This is particularly important for their prospective functioning as exhaust gas converters for biogas engines.

The quality of the in situ synthesis of MFI materials was checked by XRD analyses performed at various stages of preparation. The confirmed MFI structure of template-free material demonstrated the highest SCR activity and hydrothermal stability among the studied samples differing in Si/Al content, preparation conditions (use of organic template) and depositing method (in situ synthesis vs. dip-coating). The results of mechanical endurance tests by ultrasonication demonstrated that the adhesion of the in situ deposited layers is much higher than for the dip-coated materials.

The structure sensitivity of the reaction (grain size in SEM, Si/Al ratio) observed in this study will need further study that will cover higher selection of the samples varying in Si/Al content and preparation conditions as well as will engage more sophisticated methods for structural analyses of zeolites.

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